



FINAL TECHNICAL REPORT (1989-1992)

Synthesis of New Energetic Materials

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Contract: #89-J-3189

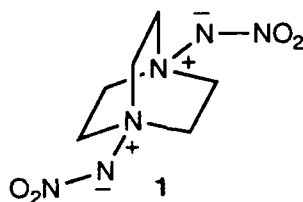
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Our work in this contract involved work only for the first year. The work could not be continued for the subsequent years due to termination of the funding and many of the proposed chemistry could not be accomplished.

(1) Synthesis of Hydrazinium Nitrates from Tertiary Amines and Their Conversion to Energetic Amine-Nitroimides

A convenient one-step preparation of hydrazinium nitrates by the reaction of tertiary amines or azaarenes with hydroxylamine-O-sulfonic acid and barium nitrate in the barium oxide was developed. The hydrazinium nitrates were easily transformed into amine-nitroimides with trifluoroacetic anhydride-trifluoroacetic acid using Katritzky's procedure including bridgehead nitrogen systems. Remarkably stable, highly energetic compounds such as DABCO-1,4-bis-nitroimide **1** were obtained in good preparative yield.



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Detailed spectroscopic and x-ray structural studies were carried out to substantiate the structures. In preliminary tests, compound **1** was found to be of high energetic nature with density 1.610 g/cc.

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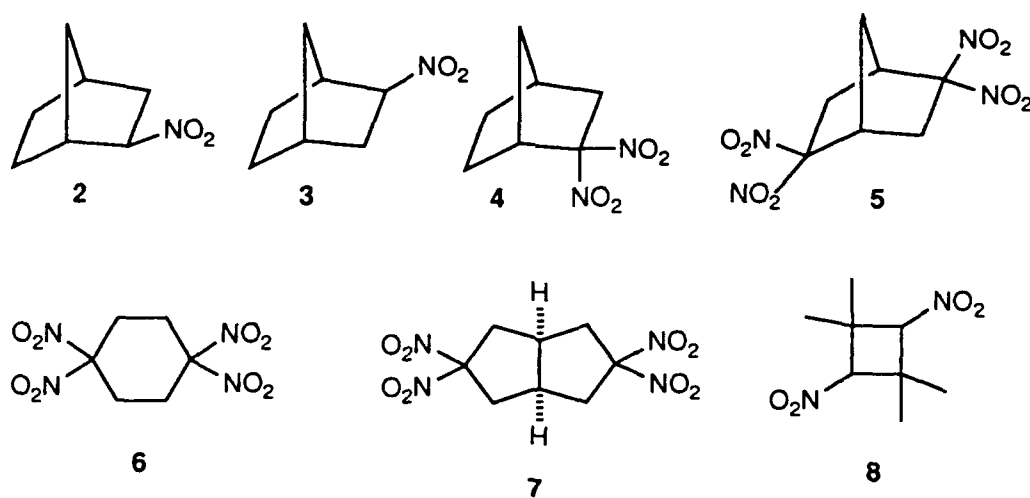


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(2) Synthesis of Polynitropolycycloalkanes

The preparation of a series of highly energetic and hitherto unknown polynitronorbornanes, bicyclooctanes and cyclohexanes was achieved. Oxidation of mono- and bis-oximinonorbornanes with peroxytrifluoroacetic acid furnished 2,5-dinitronorbornanes **2** and mononitronorbornanes **3**, whose oxidative nitration with potassium ferricyanide in the presence of sodium nitrite and sodium hydroxide gave 2,2,5,5-tetranitrobicyclo[2.2.1]heptane **4** and 2,2-dinitrobicyclo[2.2.1]heptane **5** in high yield. 3,3,7,7-Tetranitrobicyclo-[3.3.0]octane **6** and 1,1,4,4-tetranitrocyclohexane **7** were also obtained by similar oxidative nitration of the corresponding dinitro compounds in 70-80% yields. Oxidation of 1,3-dioximino-2,2,4,4-tetramethylcyclobutane, however, gave the corresponding 1,3-dinitro compound **8** in very poor yield.



The structures of polynitronorbornane, bicyclooctane and cyclohexane were determined by single crystal x-ray diffraction.

Publications Supported by ONR Grant #89-J-3189

- 1) One-Step preparation of Hydrzinium Nitrates from Tertiary Amines and Azaarenes with $\text{H}_2\text{NOSO}_3\text{H}/\text{Ba}(\text{NO}_3)_2/\text{BaO}$ and Conversion to Energetic Amine-Nitroimides, G. A. Olah, M. B. Sassaman, M. Zuanic, C. B. Rao, G. K. S. Prakash, R. Gilardi, J. Flippen-Anderson, C. George, *J. Org. Chem.* **57**, 1585 (1992).
- 2) Polynitronorbornanes, Bicyclooctanes and Cyclohexanes, G. A. Olah, P. Ramaiah, G. K. S. Prakash, R. Gilardi, *J. Org. Chem.* in press.

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